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Chloride and potassium measurement and control in the pulping and chemical recovery cycle

Scope

Considerable research and operating experience have established industry acceptance that limiting chloride and potassium concentrations in the pulping and recovery cycle liquors is necessary to achieve recovery boiler capacity and high availability. Limiting these non-process elements can result in ash deposits on boiler heat transfer surfaces that are controllable by sootblower operation. This Technical Information Paper (TIP) will provide an understanding of the sources of chloride and potassium in the mill cycle and their effect on carryover particles and fume in the recovery boiler, the steps that can be taken to develop a mill material balance and determine the maximum acceptable concentration of these in the precipitator ash, and the various approaches that can be applied to limit the concentrations. Ash produced in many recovery boilers contains alkali carbonate compounds, in addition to the sulfates, and their effect is also addressed. Note that there are many other factors that contribute to recovery boiler fouling such as: high carryover, low ash pH, and poor sootblower operation. These issues are not covered in this document. Processes are described that are available and are being developed to remove chloride and potassium from the cycle with sufficient detailed information to permit an operating mill to make a preliminary evaluation of the most suitable process (1).

Definitions

A more extensive definition of the terms following has been provided by Tran (2).

First melting temperature – the temperature at which the first liquid phase is formed in the material.

Sticky temperature – temperature at which the material contains 15 to 20% liquid phase and becomes sticky. T_{STK} or T_{15} .

Radical deformation temperature – temperature above which the material contains about 70% liquid phase and is so fluid that it can run off due to its own weight (also referred to as slagging temperature). T_{RD} or T_{70} .

Sticky temperature range – temperatures in the range between T_{STK} and T_{RD} where deposits are sticky.

Enrichment factor (EF) - a multiplier factor by which the chloride and potassium in the black liquor solids increase in the ash deposit.

TPD – tons per day of pulp production

TIP Category: Automatically Periodically Reviewed (Five-year review)



Documents

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Safety precautions

The application of the information in this TIP requires personnel to come in contact with the process liquid streams in the pulping and recovery cycle that must be handled with caution. Some of these are caustic at temperatures that can cause burns, such as, black liquor, green liquor and white liquor. Others are acidic such as spent acids from chlorine dioxide production and tall oil acidification. The mill should have Material Safety Data Sheets for these streams that describe procedures for sampling, use and disposal, and the protective attire to be worn, and these should be strictly adhered to.

Definition of chloride and chlorine as used in this document

Chloride refers to the Chloride ion as it is present in either the liquor streams or the ash. In the liquor streams Chloride would exist as a negatively charged ion (Cl^-), which is typically balanced by a positively charged ion, either sodium (Na^+) or potassium (K^+). In the ash it would be present mostly as either sodium chloride (NaCl) or potassium chloride (KCl). When using the term chlorine (Cl), this document is referring to all forms of this element, not only the chloride ion. For example an elemental analysis indicates the amount of Cl , not the amount of chloride ion in a sample analyzed. Both amounts are exactly the same, nonetheless.

Chloride and potassium in the mill cycle

The emphasis in the kraft pulp mill to reduce effluent discharge results in the retention of non-process elements in the mill recovery and pulping cycle. The concentrations increase as the effluent discharges are reduced and more are retained in the pulping and recovery cycle at equilibrium. They must either be prevented from entering the mill or separated from the cycling liquor and removed from the mill, or both.

Chloride and potassium are non-process elements in the liquor cycle of the mill. They can reach a concentration in the black liquor where they are troublesome for the operation of the recovery boiler. Their presence can have a negative impact on the availability of the recovery boiler to process black liquor. Increasing concentrations of chloride and potassium in black liquor have resulted in increased fouling of the heat transfer tube surfaces with deposits that can become hard and more difficult to be removed by the sootblowers. An increase in the chloride and potassium concentrations lowers the temperature at which the ash becomes sticky, but also increases the range of temperature in which deposits can accumulate between the sticky temperature (T_{STK}) and the radical deformation temperature (T_{RD}), thus reducing the effectiveness of sootblowers to remove the deposits.

Low first melting temperature deposition is the most significant factor contributing to corrosion of superheater tubes. Molten smelt flowing on the surface of superheater tubes generally occurs at the flue gas inlet in the lower sections of the superheater tube banks where the temperature of the gas exceeds the radical deformation, or slagging, temperature of the deposit. Considerable work on deposit properties are documented in the following reference; results of research on first melting temperature were published in 1999 (3).

The impact of chloride and potassium in the deposits on recovery boiler heat transfer surfaces has been the subject of intense study and there exists today an extensive list of literature on the subject. Only a small part of the literature is cited to an extent required for determining and interpreting the results of sample analysis, sticky temperature and the melting point of ash deposits, and processes for chloride and potassium removal.

The negative impact of the chloride and potassium in the black liquor and carryover particles resulting from liquor combustion requires consideration of alternative methods to control their levels in the mill cycle. The TIP is written for use in the pulp mill by the people working in the mill. It is designed to develop the information to establish a mill balance on chloride and potassium, to determine a limit of these in the mill cycle to enhance recovery boiler availability, to evaluate the best control process for removal of chloride and potassium from the precipitator ash, to recognize that the carbonate will affect the process selection and operation, to interpret results, and to know the simple tools for measurement and control of the operation.

Effect of chloride and potassium on boiler availability

The availability of the recovery boiler to process black liquor for chemical recovery is compromised by increased concentrations in the black liquor of Cl and K (2). The amounts of Cl and K in the deposits on boiler heat transfer surface and in the precipitator ash increase with an increase in the Cl and K concentrations in the black liquor. Interrupting the chemical recovery process to clean the boiler heat transfer surfaces can result in an incremental decrease in pulp production. Likewise, outage time to repair superheater tubes that have thinned due to corrosion can decrease production. The desirable recovery boiler operation is to be on-line from one scheduled outage to the next, generally one year, with the only cleaning required being successfully provided by the sootblowers removing ash deposits from surfaces with blowing steam jets. The information in this TIP is intended as a guide to determining for a specific set of mill conditions the Cl and K concentration in the deposits on superheater and generating bank surface below which they are easily removed by the impact of sootblower steam and above which the deposits become sticky and/or hard and are not effectively removed, to establish the related Cl and K in the precipitator as a measurement for control, and to select control measures to operate accordingly.

Sticky deposits are more difficult to remove from surfaces than non-sticky deposits. In principle, if the deposit is below T_{STK} , it is easily removed. The temperature at which deposits are sticky is lowered by increasing amounts of Cl and K. If the deposit on heat transfer surface is above T_{RD} , the material is fluid and does not build on the surface; but flows down and off the tubes. The objective is to operate the mill with equilibrium Cl and K concentrations that minimize the fraction of the convection heat transfer surface covered in sticky deposits and most importantly, to insure that the generating bank does not operate in the sticky temperature range (4). This critical temperature range usually occurs in the superheater area.

The effectiveness of sootblowers to clean the heat transfer surfaces can be further impeded by sintering of the fine fume particles that collect on the tubes. Densification of porous fume deposits results in hardening that makes more difficult the removal with sootblowers. Sintering rate of deposits from fume particles is shown to correlate with both first melting temperature, and independently, the chloride content of the fine particles (5). Increased frequency of sootblower operation may be required to remove the deposits before they harden to an extent that they cannot be removed.

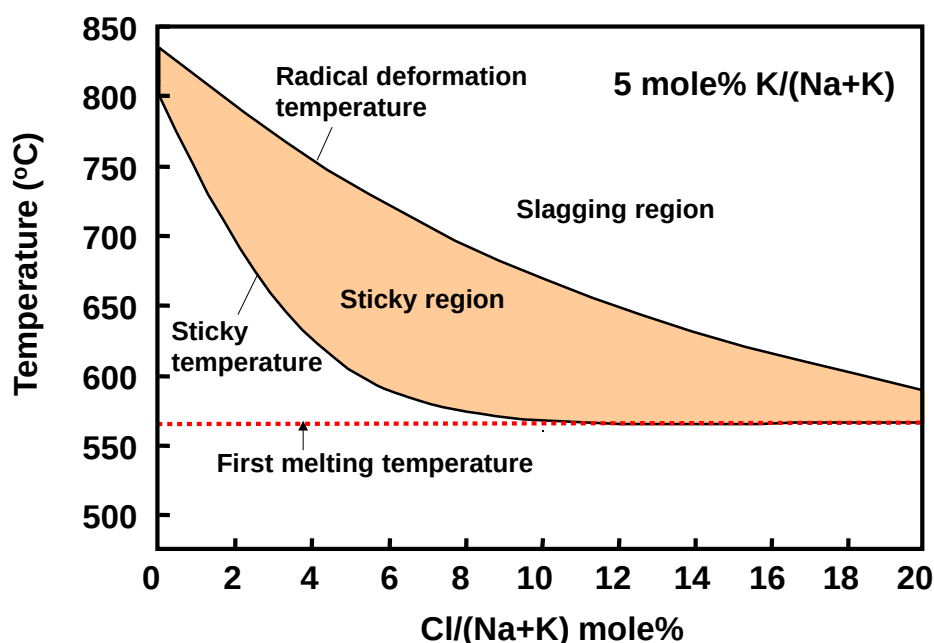


Fig. 1. Effect of chloride on carryover deposit T_{STK} and T_{RD} (2)

Figure 1 defines that a range of temperature exists over which ash deposited on the convection surface is sticky and will tend to accumulate; these deposits are difficult to remove with the sootblower steam jets. In this figure, the

sticky temperature at 5 mole percent potassium varies with the concentration of the chloride component of the ash. There is a family of curves for other potassium concentrations.

A low first melting temperature can result in the presence of liquid smelt at the outside surface of the superheater tubes. The combined effect of fluid smelt and a high tube surface temperature (primarily a result of the steam temperature in the tube) can accelerate metal loss due to corrosion. However, corrosion also occurs on a superheater tube at a moderate steam temperature where char particle carryover deposits on the tube result in local reducing conditions; it is well known that this can decrease the susceptibility of the tubes to corrosion (6). The designer can select tube metallurgy and arrange the flow path of steam through the superheater for optimum operation, but it will still be necessary to limit the Cl and K to control corrosion.

An extreme case of recovery boiler corrosion experience in Pacific coast mills with chloride concentrations in white liquor ranging from 10 g/L to 100 g/L, most of it at about 30 g/L is described in this reference (8). The experience cited is with boilers operating at relatively low pressure and steam temperature conditions of 4.24 MPa to 4.93 MPa (600 – 700 psig) and 370°C to 400°C (700 - 750°F). High chloride concentrations would result in more severe corrosion at higher pressures and temperatures. Another reference describes the experience with a closed effluent free concept in a bleached pulp mill at Thunder Bay, Ontario, where the concentration of white liquor averaged 20 g/L to 30 g/L (8). The recovery boiler operating at 454°C to 466°C (850 - 870°F) steam temperature had severe superheater corrosion after 13 months. These are cases with extreme concentrations of Cl and K that emphasize the corrosion threat of chloride as steam temperature increases. Boilers are now producing steam at >11.5 MPa (1650 psig) and >495°C (925°F) and in the future, are being installed for yet higher pressure and temperature. Control of Cl and K in the black liquor is critical for recovery boilers, and even more so for those designed to operate at high temperature and pressure for electrical generation.

Sources of chloride and potassium

The principal sources of Cl and K are wood supply and makeup chemicals entering the mill cycle. Their concentration in the pulp wood is very much dependent on the mill location and species. Hardwood typically contains a higher concentration of K than softwood (9). Chips typically have 200 ... 600 mg/kg potassium per dry wood. Because the bark has typically 1400 ... 2200 mg/kg potassium per dry bark then poor debarking can increase potassium input to the mill. Wood harvested from coastal areas generally has a higher content of Cl than wood from inland sources. It is a practice in some coastal areas to transport logs to the pulp mill by water rafting and storage with an obvious effect of increasing the chloride concentration in the wood supply. However, in general, the pulp mill has no control of potassium or chlorides in the pulp wood. The concentration of potassium in the cycle is largely established by the content in the wood supply. The water supply is infrequently a source of Cl and K. However, there are exceptions. There is one mill where water from drilled wells was high in Cl because the wells extended under the ocean and there was seepage of salt water into the wells.

Makeup chemical is purchased to provide sodium and sulfur to replace these chemicals that are lost from the mill cycle in the pulp product, to the sewer or discharged from the recovery boiler stack. Caustic soda (NaOH), or “caustic,” is available with various levels of chloride; chemical grade caustic is available with very low chloride content. Salt cake (Na₂SO₄) is also sourced with different degrees of purity. Sodium hydrosulfide (NaHS), which is used widely by bleached pulp mills for sulfidity control, is available as a chemical plant product or as a byproduct of oil refineries, with the refinery byproduct containing a wide range of non-process elements. Other sources of sodium and sulfur for makeup are at times available from nearby industrial plants looking for opportunities to dispose of their waste streams ranging from utility power station stack scrubber effluent to caustic used in the manufacture of carpet yarn.

The mill must exercise control over the chloride content of makeup chemicals entering the cycle. Makeup caustic is frequently a major source of chloride. Chemical with lower Cl concentration can be purchased albeit at higher cost. Caustic makeup from diaphragm processes can have a residual Cl content of 1 to 2% (10,000 to 20,000 ppm) as compared to caustic from a membrane process or mercury cell with less than 50 ppm chloride. The economics of purchasing higher quality chemical for control can be compared with the cost of removing the Cl and K from the mill cycle.

The substitution of soda ash (Na_2CO_3) for caustic as the source of sodium makeup is an alternative that warrants consideration. This could be an attractive approach in a mill that has excess causticizing system and lime kiln capacity. However, this process substitution would not be considered in a pulp mill where the lime kiln capacity limits production. The financial evaluation of Na_2CO_3 as makeup requires consideration of the increased amount of auxiliary fuel that would be used in the lime kiln.

Most bleached pulp mills generate chlorine dioxide (ClO_2) on the mill site. The process effluent is a spent acid containing sodium and sulfur that is neutralized and used as a source of makeup chemical in the mill cycle. The effluent normally contains low levels of Cl, but higher concentrations are possible if the ClO_2 generation is not optimal or the system requires maintenance.

There are other sources of sodium and sulfur in individual mills that are frequently added to the black liquor incinerated in the recovery furnace, such as, soap, acidic tall oil brine and effluent from a power boiler scrubber. The tall oil brine and the ClO_2 plant effluent are usually neutralized with caustic, which may include chlorides.

A common process for ClO_2 production is the R8 process that reacts sulfuric acid and methanol with salt cake (Na_2SO_4). An effluent by-product is sodium sesquisulfate acid [$\text{Na}_3\text{H}(\text{SO}_4)_2$]. For each ton of ClO_2 produced, the effluent is an equivalent of 1.3 tons of $\text{Na}_3\text{H}(\text{SO}_4)_2$ solution, in which there is residual chloride. The newer R10 process operates with less Cl in the byproduct having about 1.1 ton of Na_2SO_4 crystals per ton of product ClO_2 . The R10 process also has an advantage of a lower sulfur to sodium ratio in that each mole of sodium in the crystals carries with it one-half mole of sulfur whereas the R8 effluent brings to the cycle two-thirds of a mole of sulfur for each mole of sodium. The effect is that the R10 byproduct used as makeup puts less pressure on elevating the sulfidity than does the R8 product.

The R10 process offers additional advantages to the mass balance in the mill pulping and recovery cycle. A further reduction in chlorides can be achieved by washing the crystals before mixing them into the black liquor. Also, as the byproduct does not need to be neutralized as is the requirement with the $\text{Na}_3\text{H}(\text{SO}_4)_2$ solution, the amount of caustic required for neutralization is eliminated, thus eliminating a source of chloride.

There is another alternative to investigate for the R8 process. This is to substitute hydrogen peroxide for the methanol that is widely used as the reducing agent in the ClO_2 generators (10). The result of using the hydrogen peroxide is a decrease in the quantity of salt cake available for mill makeup. This could be particularly attractive for a mill already generating hydrogen peroxide for the bleach plant.

Obtaining samples for determination of chloride and potassium concentration

Ash samples for the determination of chloride and potassium values that are used in a mill balance and to establish the requirements for the removal process are generally preferred to be collected at one of the electrostatic precipitator discharge chutes. The sample point should be located downstream of the seal valve that prevents a back flow of air into the precipitator. The practice is to install a small door or a short pipe nipple with a large valve at the sample location. The opening should be large enough that a ladle or cup can be inserted into the chute to “catch” the sample. The quantity of sample required for analysis is about 150-200 ml (1 pint). Where conditions make it possible, a sample should be collected from each of the precipitator chambers and the equal quantities mixed thoroughly to prepare a representative sample for analysis. However, other locations are acceptable, such as, the discharge from an economizer hopper ash conveyor. Avoid taking a sample from the final electrical field of a chamber as the fine ash at this point may be enriched in chloride.

There is no steadfast rule for sampling and analysis frequency. Some considerations for obtaining ash samples for analysis are:

- Obtain samples when the boiler has been operating steady at a constant liquor flow for several hours (4 hours is good).
- Once a month obtain samples during operating periods when the sootblowers are effective in maintaining clean surfaces. Surfaces that are accumulating deposits can be observed to have gas side increasing pressure drop and/or decreasing superheater steam temperature.
- For a mill producing both hardwood and softwood pulp, occasionally analyze samples for both.

- At any time that a black liquor sample is to be collected and analyzed for elemental composition, for example, for boiler performance calculations, obtain an ash sample. The relative Cl and K concentrations between the precipitator ash and black liquor yields an enrichment factor, which if abnormally high, suggests to make changes in the black liquor burning. An enrichment factor will be needed for the mass balance of the cycle to calculate alternative processes.
- If there is an increase in the mill sulfidity level, more SO₂ may be formed in the furnace.
- With high SO₂ levels (>50 ppm), it may be necessary to make more frequent analysis of the black liquor or the white liquor for Cl content as a control measure. Variations in SO₂ will cause variability in the Cl content of the precipitator ash due to reactions between SO₂ and alkali chlorides (NaCl and KCl) to form HCl (11). Therefore, with high SO₂, an assessment of the mills requirement for Cl and K removal should be based on the Cl levels in actual recovery boiler deposits as precipitator ash chloride levels may not be well correlated with deposit chloride levels.

Measurement of Cl in white and green liquors

Monitoring the chloride levels in liquors and inferring the chloride content of recovery boiler carryover and electrostatic precipitator (ESP) ash levels (and the resultant sticky temperature) can be done effectively by using either the chloride content of green liquor or white liquor. There are a variety of ways to do this by using either wet chemistry methods or by the use of ion specific electrodes. As pointed out above this will eliminate the variability due to fluctuations in SO₂ levels in a recovery boiler and will also reduce the variability due to short term changes on the recovery boiler.

Cl and K in ESP ash

Table 1 shows data on chloride (Cl) and potassium (K) levels in ESP ash from 30 different kraft pulp mills in Canada, the United States, Brazil and Scandinavia, in the ascending order of Cl. The Cl content in the ash varies significantly from mill to mill, from less than 1 wt% Cl (Mills #1 to 5) to over 10 wt% Cl for coastal mills (Mills #27 to 30). The potassium content also varies but not as much as chloride. It typically ranges between about 4 to 10 wt% K, depending on the wood species used in individual mills. ESP ash from hardwood mills tends to contain more K than that from softwood mills.

ESP ash consists of mostly sodium (Na), potassium (K), chloride (Cl), sulfate (SO₄) and carbonate (CO₃). The total amount of these constituents should be close to 100 wt%, with a tolerance of ± 2 wt%. Furthermore, in a perfect ionic system, the negatively charged ions (anions) should be balanced by the positively charged ions (cations). This means that the anions-to-cations (-/+) molar ratio of the ash should not deviate from 1 more than ± 0.05 . Impurities in the ash can cause some deviation in the total. The variance in the charge balance has some scatter, possibly reflecting the cumulative deviation for analyzing each constituent.

Calculation of -/+ molar ratio

Below is an example for calculating the -/+ molar ratio of the precipitator ash from Mill #16 which has a typical Cl content of about 2.5 wt% Cl. Note that since Na⁺, K⁺ and Cl⁻ are monovalent (single-charged), their atomic weights must be multiplied by 2 to obtain a molecular weight that matches the divalent (double-charged) SO₄²⁻ and CO₃²⁻. The molecular weights of Na₂, K₂ and Cl₂ are respectively 23 x 2 = 46, 39.1 x 2 = 78.2, and 35.5 x 2 = 71. Thus,

$$-/+ \text{ molar ratio} = \frac{\sum \text{anions}}{\sum \text{cations}} = \frac{\text{Cl}_2 + \text{SO}_4 + \text{CO}_3}{\text{Na}_2 + \text{K}_2} = \frac{2.53/71 + 53.1/96 + 7.50/60}{31.1/46 + 4.96/78.2} = 0.96$$